Supplementary information

Low-Grade Waste Heat Recovery for Wastewater Treatment Using Clathrate Hydrate Based Technology

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Experimental Methods

Materials and Apparatus

The detailed information about the chemicals used in the experiment is shown in Table 1.

Table 1. The detailed information about the chemicals used in the experiment

Materials	**Chemical formula**	**Purity**	**Supplier**
Hexahydrate chromium trichloride	$CrCl_3 \cdot 6H_2O$	99.0%	Xilong Chemical Industry Incorporated Co., Ltd., Guangdong Province, P.R.C.
Nickel sulfate hexahydrate	$NiSO_4 \cdot 6H_2O$	98.5%	Damao Chemical reagent Factory, Tianjin City, P.R.C.
Zinc sulfate heptahydrate	$ZnSO_4 \cdot 7H_2O$	99.5%	Xilong Chemical Industry Incorporated, Co., Ltd., Guangdong Province, P.R.C.
Copper sulfate pentahydrate	$CuSO_4 \cdot 5H_2O$	99.0%	Bodi Chemical Industry Incorporated Co., Ltd., Tianjin City, P.R.C.
Methylene blue	$C_{16}H_{18}ClN_3S$	99.95%	J & K Scientific, Beijing, P.R.C.
1,1,1,2-Tetrafluoroethane	$C_2H_2F_4$	99.99%	Shandong Dongyue Chemical Co., Ltd., P.R.C.

The stimulated wastewater was prepared by adding a certain amount of methylene blue, hexahydrate chromium trichloride (CrCl3•6H2O, 99.0%), nickel sulfate hexahydrate (NiSO4•6H2O, 98.5%), zinc sulfate heptahydrate (ZnSO4•7H2O, 99.5%), copper sulfate pentahydrate (CuSO4•5H2O, 99.0%) to deionized water. The high-pressure chamber made from stainless steel (maximum 20 MPa designed pressure) and was manufactured by Shandong Zhongshi Dashiyi Technology Co., Ltd. P.R.C. The temperature of the chamber was controlled using a water bath (XT5718RCE800L, Xutemp, Hangzhou, Co., Ltd.) with an accuracy of ±0.1 K and a temperature varying from 258Kto 323K. Three thermocouples (Yamari Industries, Japan) with precisions of

± 0.1 K, were inserted into the sides of the chamber to monitor the temperature trajectories. A pressure transducer (Nagano Co., Ltd., Japan) was connected to the top of the cell to measure pressures in the range of 0-2.5 MPa with a precision of ±0.01 MPa. Two electric heater with 0-100 W were used to simulate the low grade waste heat. Two types of simulated wastewater were prepared: organic wastewater (100mg/L MB), organic- heave metal wastewater (100mg/L MB, each heavy metal ion 100mg/L).

Method

The 4000ml of simulated wastewater is added to the chamber. The temperature of the chamber was controlled by water bath at 275K. R134a gas was injected into chamber at 0.5 MPa when the temperature of chamber decreased to 275K. After that, the electric heaters were opened to heat the liquid R134a until the bottom temperature in liquid was near 281K. Then, the electric heaters were turned off. During heating process, massive hydrates formed.

Following the completion of the hydrate formation, solid-liquid separation was performed through vacuum filtration or centrifugation. The hydrate was then transferred to a decomposer, where decomposition into water and R134a occurred at 298K. Finally, treated waster and R134a could be obtained.

Measurements and Analysis

The concentration of MB was determined through wavelength scanning within the range of 530−720 nm using a UV/Vis/NIR spectrophotometer (Lambda750S, USA). Calibration was conducted to establish the correlation between the UV absorption intensity and the concentration of MB, depicted in Fig. S1. The primary absorption band (λ_max) of MB resides at 664 nm. Absorption spectra were measured for aqueous solutions of MB at various concentrations (0-4.5 mg/L). The calibration curve (R^2=0.999) illustrating the relationship between absorbance and concentration is presented in Fig. S1b. If the concentration exceeds the detection limit, the sample is initially diluted to an appropriate concentration range and then measured using the UV-Vis-NIR spectrophotometer. The calibration curve equation accurately calculates the concentration of MB in the sample. The concentration of metal ions was determined using an inductively coupled plasma spectrometer (ICP, AVIO 500, PerkinElmer, USA). Each sample was subjected to 2-3 detections by the ICP. The average value and error bars were calculated and are depicted in Fig. 4. The error bars represent the standard deviation.

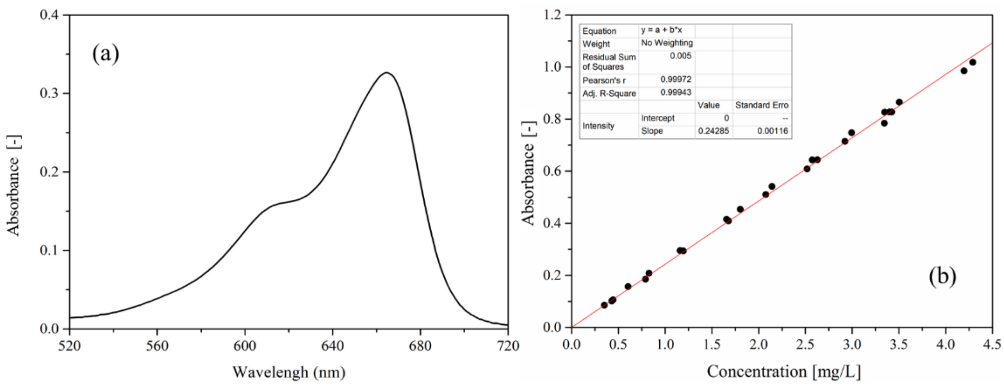

Fig. S1 (a) the absorption band of MB (b) The calibration curve of UV absorption spectra of aqueous solutions of MB at various concentrations.

Calculation

Removal efficiency for wastewater

Based on the concentrations of MB or heave metal ions measured, the removal efficiency was calculated as follows[1-3]:

$$\text{Removal Efficiency} = \frac{C_i - C_d}{C_i} \times 100\% \tag{1}$$

where C_i and C_d are the concentrations of MB or heave metal ions in the simulated wastewater and water from the decomposition. The C_d includes water obtained from decomposition through vacuum filtration or centrifugation.

Energy utilization efficiency for low grade waste heat

The Figure S2 shows the schematic diagram of the bottom heater structure of the chamber. The angle is 165°. Thus, the theory energy utilization efficiency can reach 51.4%.

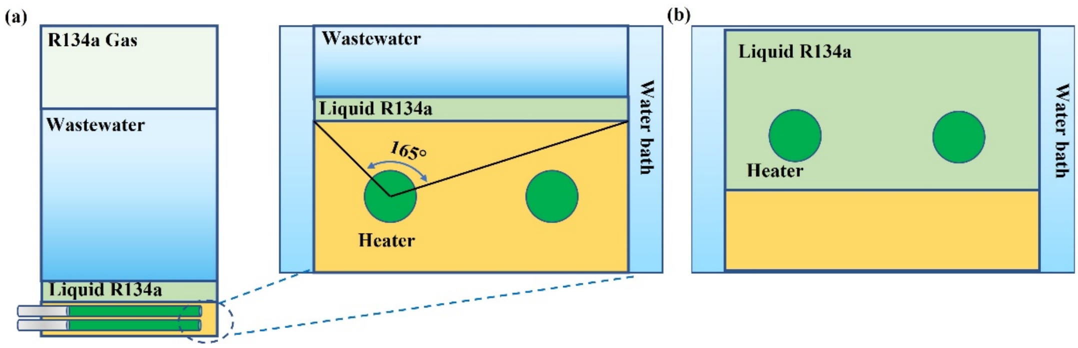

Figure S2 (a) schematic diagram of the bottom heater structure of the chamber. (b) The improved structure of heater in the future can enhance the energy utilization efficiency for low grade waste heat.

References

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